

## Investigation of Zero-Field Splitting Parameters in Spin Triplet Transition Metal Complexes

Fataftah, M.S., Collins, K.A. and Freedman, D.E. (Northwestern U., Chemistry)

### Introduction

The emerging paradigm of quantum information science (QIS) has the potential to impact areas all across science. Electronic spins are attractive qubit candidates, featuring numerous recent advances[1]. Single qubit addressability represents the next frontier for molecular based qubits [2]. Towards this goal, we are targeting molecular mimics of the  $S = 1$  nitrogen vacancy center in diamond that features an electronic structure that enables optical addressability at single spin level [3]. To this end, we are synthesizing spin triplet  $1^{st}$  row transition metal complexes in trigonal ligand fields that feature EPR addressable transitions, necessitating fine-tuned control over zero-field splitting (ZFS). To this end, we synthesized complexes of Cr(IV) and Ni(II) in trigonal ligand fields and investigated their ground state ZFS parameters via high-field, variable frequency electron paramagnetic resonance spectroscopy (HFVF EPR), a prerequisite to investigating their excited state and electronic spin relaxation dynamics to nominate them as potential qubit candidates [4].

### Experimental

Microcrystalline powders were prepared under a dinitrogen atmosphere in polyethylene vials capped with a Teflon stopper. Cw EPR measurements were performed on a variable frequency EPR spectrometer with a 15/17 T superconducting magnet in the EMR Facility of the National High Magnetic Field Laboratory. EPR spectra were collected at frequencies in the range of 64 GHz to 412 GHz, at temperatures ranging between 5 K and 30 K.

### Results and Discussion

Cw EPR spectra were collected for a series  $S = 1$   $\text{Cr}^{4+}$  complexes in trigonal bipyramidal geometries, with variable halide donors including  $\text{F}^-$  (**1**),  $\text{Cl}^-$  (**2**),  $\text{Br}^-$  (**3**), and  $\text{I}^-$  (**4**) (**Fig.1a**). Fitting the HFVF EPR spectra reveals a smooth variation in  $D$  across the series, with  $D$ -values of 5.2, 5.6, 6.4, 7.3  $\text{cm}^{-1}$  for **1–4**, respectively. These results suggest  $d^2$  electronic configurations in  $\text{Cr}^{4+}$  complexes are addressable by W-band (94 GHz) frequency to investigate their coherence properties. The small variation in  $D$  across the series enables investigation of the heavy atom effect on electronic relaxation dynamics (intersystem crossing) without compromising their EPR addressability.

We also investigated the pseudo-octahedral  $\text{Ni}^{2+}$  complex (**5**) by HFVF EPR spectroscopy. Fitting the data presented in **Fig.1b** revealed small, yet rhombic ZFS splitting parameters suggesting it be interrogated by Q-band (33 GHz) EPR and nominates it as a potential electronic spin qubit. More importantly, the  $D_{3d}$  molecular symmetry induced rhombicity and enables multiple addressable EPR transitions within a single electronic ground state.

### Conclusions

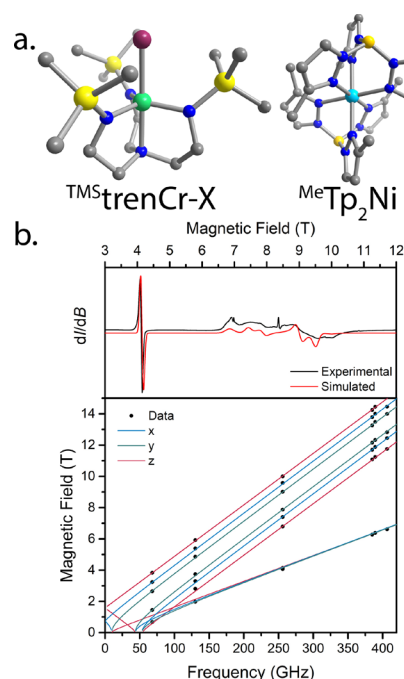
Accessing EPR addressability in  $S = 1$  compounds represents a new synthetic challenge of inorganic chemists, necessitating thorough magneto-structural correlations. This work represents the initial steps towards targeting single spin addressability in molecular electronic spin qubit candidates. Future work on the NHMFL will involve investigating their spin relaxation dynamics ( $T_1$  and  $T_2$ ) to determine their viability as electronic spin qubit candidates.

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### References

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**Fig.1 a** Molecular structures of the TMStrenCrX series of complexes (left) and  $\text{MeTp}_2\text{Ni}$  complex (right). **b.** Cw EPR spectrum of  $\text{Ni}(\text{MeTp})_2$  collected at 256 GHz (top) and fits to the high-field, variable frequency EPR data (bottom). Fits to the data yield  $D = -1.61 \text{ cm}^{-1}$ ,  $|E| = 0.16 \text{ cm}^{-1}$  and  $g$ -values of [2.15, 2.155, 2.169].